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Tennessee Agricultural and Industrial State University
Nashville

Contract: N9onr-95700

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"Preparation and Properties of Organic
Derivatives of Tin Hydride"

Final Report

C. R. Dillard in collaboration with E. E. Holmes,
J. R. Lawson, D. E. Simmons, and J. B. Yeldell

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I. INTRODUCTION

The goals of the research project sponsored by the Office of Naval Research at Tennessee Agricultural and Industrial State University are as follows:

(1) to prepare and study the properties of a number of organic derivatives of tin hydride, (stannane).

(2) to deduce from the differences between the properties of these compounds and those of analogous compounds of carbon and silicon; the effects due to the more electropositive nature of tin.

(3) to derive, wherever possible, theoretical principles which will serve as a guide to further research in this area.

The approach to this research has been dictated by the availability of apparatus and personnel, hence the choice of problems appears arbitrary. However, as the data from various experiments have been assembled, certain consistencies have become apparent. These consistencies are discussed in the final section of this report where the results of the various experiments are correlated and interpreted in the light of recent chemical theory.

II. THERMOCHEMISTRY OF SEVERAL ALKYL AND ARYL STANNANES

It is desirable to make thermochemical studies of organo-tin compounds because the data obtained can be used to calculate bond energies and the electronegativity of the metal. This information is important in that it will contribute to the theoretical interpretation of the chemical properties of organo-tin compounds.

Published values of the heats of combustion and formation of tin alkyls exist only in the case of tetraethyl tin, tetrapropyl tin, tetrabutyl tin and tetraamyl tin.[1]

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[1] W. J. Jones, D. P. Evans, T. Gulwell and D. C. Griffiths, J. Chem. Soc. 39-47 (1935)

In this investigation, the heats of combustion and formation of tetraethyl tin and tetrabutyl tin have been redetermined, and the heats of combustion of tetramethyl tin, tetra-n-hexyl tin and tetraphenyl tin are reported for the first time.

Experimental

Pure tetra alkyl stannanes were prepared according to the method of Kocheshkow[2] as modified by Jones and co-workers.[1] Ben-

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[2] K. A. Kocheshkow, J. Gen. Chem., (USSR) 4, 1359 (1934)

---

zene solutions of stannic chloride were added to an excess of the appropriate grignard reagents. The excess grignard reagent was then destroyed by hydrolysis and the crude product was repeatedly distilled through an efficient fractionating column until a sample was obtained which showed no change in refractive index upon further distillation. (It was found that the index of refraction was a better criterion of purity than elementary analysis. Samples containing small amounts of impurity often gave "correct" analyses but in such cases, the observed index of refraction would change upon further distillation.)

In the preparation of tetramethyl tin, toluene rather than benzene was used as a solvent for the stannic chloride in order that the separation of the product could be more easily accomplished.

Tetraphenyl tin, a solid at room temperatures, was purified by

recrystallization from benzene.

Physical properties of the compounds studied are listed in Table I.

TABLE I

Physical Constants of Compounds Studied

Compound	B. Pt. °C	M. Pt. °C	n_D^{20}	Density at 20° C g/ml
Tetramethyl tin	78°/760mm		1.4413	1.2905
Tetraethyl tin	78°/13mm		1.4724	1.1916
Tetrapropyl tin	81°/4mm		1.4830	
Tetrabutyl tin	145°/10mm		1.4730	1.057
Tetraamyl tin	181/10mm		1.4733	1.0206
Tetra-n-hexyl tin	209°/10mm		1.4743	0.9950
Tetraphenyl tin		224°		0.432

The heats of combustion were determined in a Parr oxygen bomb calorimeter, model no. 13051. The bomb was a single valve self-sealing type constructed o. illium. Its assembled weight was 2963.7 grams and its internal capacity was 350 cc.

The bomb was held in an oval calorimeter bucket of slightly more than 2000 cc. capacity. This in turn was contained in a plain, double walled bakelite jacket. The heat of stirring was within the limits of experimental error, moreover, this effect was eliminated by running the standardizations and determinations in exactly the same manner.

The temperature was measured by means of a precision thermometer, (certificate No. R0229), reading from 65 to 95° F.,

graduated in hundredths of a degree, and standardized by the Parr Instrument Company according to the recommendations of the National Bureau of Standards. The maximum error in differential measurements within any ten degree range was one hundredth degree Fahrenheit (0.01° F). The observed temperature rise in a combustion experiment was converted from degrees Fahrenheit to degrees Centigrade using the factor, 1° C $= 1.8^\circ$ F.

The charge was fired by ten centimeters of special resistance fuse wire of such dimensions that each one centimeter length burned was equivalent to 2.8 calories.

The same mass of water, within 0.1 gram, was used in each combustion. This was measured in a two liter volumetric flask at a temperature of 27° C. maintained constant by placing the flask in a thermostated water bath. The same pressure of commercial oxygen, 25 atm. absolute, was used in every run, and 1 g. of water was added to the bomb.

Nitric acid formed in the combustion[#] was determined by titration of the bomb washings with standard sodium carbonate, using methyl orange as indicator.

The actual temperature rise during combustion was calculated and corrected according to the method of Dickinson.[3]

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[3]Dickinson, H. C., Bull. U. S. Bur. Stds. 11, 189 (1915).

_____

The calorimeter constant was determined by the combustion of

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[*]Nitric acid was formed by the combustion of residual nitrogen in the bomb. It was found that the combustion reactions proceeded more smoothly when the bomb was not flushed with oxygen prior to the final filling.

benzoic acid (standard sample 39 g.) supplied by the National
Bureau of Standards. The isothermal heat of combustion of this
sample is certified to be 26.4388 abs. kj. **per** gram true mass
when burned in pure oxygen at 25-30 atm. pressure in a bomb of
approximately 1/3 liter volume. For convenience in these measure-
ments, the calorimeter constant was expressed in calories per de-
gree, derived from the international kilojoule by using the con-
version factor; 1 calorie = 0.0041840 abs. kj.

The value of the calorimeter constant was found to be 2421 ≮ 2
cal. per degree. Detailed calibration data is given in Table II.

TABLE II

Standardization of the Bomb Calorimeter

Run No.	Calorimeter Const. (cal/degree)
1	2427
2	2415
3	2428
4	2417
5	2420
Mean	2421 ≮ 2.1

Samples of the tetra-alkyl stannanes were weighed directly in
the sample cup of the bomb and the procedure used in the determina-
tion of their heats of combustion was identical with that used in
the standardization of the calorimeter.

A slight modification was adopted in the case of the highly
volatile tetramethyl tin. Samples of this compound were weighed

and sealed in soft glass ampoules. A 0.5 gram pellet of benzoic acid was placed in the bomb with each sample to insure breakage of the ampoule and to initiate the combustion of the tetramethyl tin. In the calculations of the heat of combustion, corrections were made for the heat due to the benzoic acid.

The solid tetraphenyl tin was compressed into pellets weighing approximately one gram.

In most of the experiments, the combustion reaction went to completion as was evidenced by the consistent results and by the fact that stannic oxide was left as a white residue. In cases where the residue was dark or discolored, it was obvious that the combustion had been incomplete.

Calculation of Heats of Combustion

Combustion data on the compounds investigated are given in Table III. In order to express the experimental results in calories per mole under the conventional conditions of temperature and pressure, the following corrections were applied:

(i)   All weighings were reduced to weight in vacuo.

(ii)   The bomb process was corrected for the combustion of the fuse wire and formation of nitric acid.

(iii)   The bomb process was corrected to constant temperature.

(iv)   The pressure was reduced to one atmosphere.

(v)   The combustion was converted from a constant volume process to one of constant pressure.

Correction (i) was applied at the outset. This required the knowledge of the densities at room temperature of all the substances weighed. Reliable figures were available for all of these except tetraphenyl tin, in which case the density was measured and found to be 0.432 g/ml.

TABLE III

Heats of Combustion and Formation

of

Tetra-organo-tin Compounds

Compound	Observed $-\Delta H$ (comb.) Kcal/mole	Heat of formation Kcal/mole
Tetramethyltin	945 927 929 934 Mean 934 $\not< 2.8$	- 9
Tetraethyltin	1541 1548 1552 1547 Mean 1547 $\not< 1.5$ (1521)[a]	$\not< 27$ ($\not< 39$)[a]
Tetra-n-butyltin	2824 2806 2819 Mean 2816 $\not< 3.9$ (2773)[a]	$\not< 57$ ($\not< 111$)[a]
Tetra-n-hexyltin	4063 4065 4050 Mean 4060 $\not< 3.2$	$\not< 119$
Tetraphenyltin	3178 3175 3189 3184 3182 Mean 3182 $\not< 1.8$	$\not< 581$

[a]Data of Jones and co-workers, ref. 1.

Correction (ii) was determined by measuring the unburned wire
and by titrating the nitric acid formed in the reaction with stand-
ard sodium carbonate.

The initial temperature of most of these experiments was ap-
proximately 27° C., which was about two degrees below average room
temperature. The heat of the actual bomb process was corrected to
this temperature rather than 25° using the equation suggested by
Washburn.[4]

[4]Washburn, J. Res. Nat. Bur. Stds. 10, 525 (1933).

The observed heat of the bomb process was corrected to the heat
of combustion at one atmosphere pressure with all of the substances
in their standard states, according to the method of Washburn[4] (loc.
cit.). In the case of the compounds studied in this investigation,
this correction was well within the limits of experimental error.

Correction (v) was computed according to the equation,

$$\Delta H = \Delta U_r + \Delta nRT$$

where ΔH is the heat of combustion at constant pressure, ΔU_r is
the corrected heat of combustion at constant volume, Δn is the
change in the number of moles of gaseous substances involved in the
combustion reaction, R is the gas constant and T is the absolute
temperature. The general equation for the combustion of the com-
pounds studied in the investigation[*] is $(C_n H_{2n+1})_4 Sn +$
$(6n+2) O_2 \longrightarrow SnO_2 + 4n CO_2 + (4n+2) H_2O$ and at room tempera-

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[*]With the exception of tetraphenyl tin; the equation for
the combustion of this substance is

$$(C_6H_5)_4 Sn + 30O_2 \longrightarrow 24CO_2 + 10H_2O + SnO_2$$
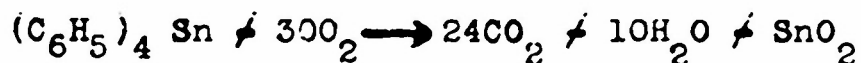
ture; $\triangle n = (6n \neq 2) - 4n = 2n \neq 2.$

The values of $-\triangle H$ listed in Table III represents the heat liberated when one mole of the given substance in its standard state burns in oxygen at one atmosphere pressure, the process occuring at approximately 27° C. These values have uncertainties of 0.1 to 0.3% which is the maximum precision obtainable with apparatus of the type used in this investigation. However, much of the thermochemical data used to calculate heats of formation and bond energies are known with no greater accuracy.

Calculation of the Heats of Formation

The heats of formation were calculated from the heats of com-bustion and the results are given in Table III. In these calcu-lations the heats of formation of liquid water, gaseous carbon dioxide and solid stannic oxide were taken to be 68.317^{5}, 94.052^{6}, and 138.8^{7} kcal. per mole, respectively.

[5] D. D. Wagman, J. E. Kilpatrick, W. U. Taylor, K. S. Pitzer and F. D. Rossini, J. Res. Nat. Bur. Stds. 34, 143, 1945.
[6] E. J. Prossen, R. S. Jessup and F. D. Rossini, J. Res. Nat. Bur. Stds. 33, 447 (1944)
[7] J. Moose and S. W. Parr, J. Am. Chem. Soc. 46, 2656 (1924)

Discussion of Results

Comparison of the heats of combustion of tetraethyl tin and tetrabutyl tin reported by Jones and co-workers[1] (loc. cit.), with the values obtained in this investigation reveals that the results are consistently higher in the latter case. This difference is greater than that expected for a small difference in reference temperature. However, since the previous report does not include any experimental details, other than a brief description of the calorimeter, it is not possible to ascertain reasons for the ap-parent discrepancies.

The principal source of error in experiments of this type, where one of the combustion products is a solid, is failure to obtain complete combustion. This would lead to low values of the observed heat of combustion.

Inspection of Table III reveals that there is about 158 kcal per mole increase in the heat of combustion per CH_2 group added in lengthening the alkyl radical chains from methyl to hexyl. This is in agreement with the increase of 157.5 kcal per CH_2 group observed in the heats of combustion of homologous paraffin hydrocarbons.

III. CALCULATION OF BOND ENERGIES

In the case of diatomic molecules, the term "bond energy" is defined as the energy required to dissociate the molecule into its atoms. Such energies can be determined directly by spectroscopic or by thermochemical means. In the case of polyatomic molecules, it is not possible to unambiguously define the "bond energy" because of the undetermined influence of the several bonds upon one another. Moreover it has been pointed out that the electronic energy levels of the atoms in a compound may be different from the ground states of the isolated atoms.[8] Unfortunately, data con-

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[8] L. H. Long and R. G. W. Norrish. Phil. Trans. Roy. Soc., London A 241, 587 (1949).

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cerning these excited electronic states are not always available.

In the case of polyatomic molecules in which all the bonds are alike, one can determine the energy required to break all of the bonds and by dividing by the total number of bonds broken, obtain an "average bond energy" which represents a lower limit to the true

bond energy.[9]   Rough values of the bond energies of polyatomic

L. Pauling, "Nature of the Chemical Bond". Cornell Univ. Press, Ithaca, 1940 pp. 52-58.

molecules containing unlike bonds may be determined by subtracting known bond energies from the energy required to totally dissociate the molecules into atoms.

Using Pauling's empirical values of single bond energies and heats of atomization[9], together with the thermochemical data obtained in this investigation, we have calculated the tin-carbon bond energies in tetramethyl tin and tetraethyl tin. The required data is summarized in Table IV.

TABLE IV

Data Used In The Calculation of Bond Energies

| Process	ΔH_{298} (Kcal)/mole
ΔH formation $(CH_3)_4Sn$	-9.
ΔH formation $(C_2H_5)_4Sn$	27.
ΔH vaporization $(CH_3)_4Sn$ [a]	- 7.5
ΔH vaporization $(C_2H_5)_4Sn$ [b]	- 9.5
Sn(solid) $\longrightarrow$ Sn(gas) [c]	78.0
C(graphite) $\longrightarrow$ C(gas) [c]	124.3
H_2(gas $\longrightarrow$ 2 H(gas) [c]	51.7
Empirical bond energy, D(C - H) [c]	87.3
Empirical bond energy, D(C - C) [c]	58.6

(a) estimated from vapor pressure data
(b) estimated using Trouton's rule
(c) L. Pauling, reference 9

Calculations of the bond energies were made as follows:

	ΔH
$Sn(CH_3)_4$ (liquid) $\longrightarrow$ Sn(solid) + 4 C(graphite) + $6H_2$(gas)	- 9.0
$Sn(CH_3)_4$ (gas) $\longrightarrow$ $Sn(CH_3)_4$ (liquid)	- 7.5
Sn(solid) $\longrightarrow$ Sn(gas)	+ 78.0
4C(graphite) $\longrightarrow$ 4C(gas)	+ 497.2
$6H_2$(gas) $\longrightarrow$ 12 H(gas)	+ 620.4

$Sn(CH_3)_4$ (gas) $\longrightarrow$ Sn(gas) + 4 C(gas) + 12 H(gas)   +1179.1
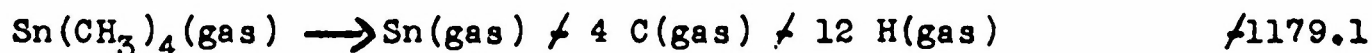
Subtracting the energy of twelve C-H bonds, (1047.6 kcal), and

dividing the remainder by four, yields 32.9 kcal/mole as the energy

of the Sn-C bond in tetramethyl tin.

In the case of tetraethyl tin the thermochemical equations are as

follows:

	ΔH
$Sn(C_2H_5)_4$ (liquid) $\longrightarrow$ Sn(solid) + 8 C(graphite) + 10 H_2(gas) + 27.0	
$Sn(C_2H_5)_4$ (gas) $\longrightarrow$ $Sn(C_2H_5)_4$ (liquid)	- 9.5
Sn(solid) $\longrightarrow$ Sn(gas)	+ 78.0
8 C(graphite) $\longrightarrow$ 8 C(gas)	+994.4
10 H_2(gas) $\longrightarrow$ 20 H(gas)	+1034.0

$Sn(C_2H_5)$ (gas) $\longrightarrow$ Sn(gas) + 8 C(gas) + 20 H(gas)   2123.9
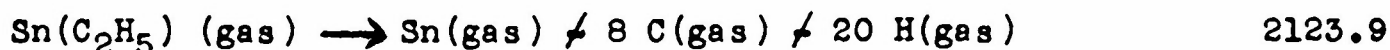
Subtracting the energies of four C-C bonds (234.4 kcal), plus twenty

C-H bonds (1746 kcal) and dividing the remainder by four, yields

35.9 kcal/mole as the Sn-C bond energy in tetraethyl tin.

Similar calculations yielded 37 kcal/mole and 39 kcal/mole as

the Sn-C bond energies in tetrabutyl tin and tetrahexyl tin, re-

spectively. However, these latter figures represent small differ-

ences between relatively large numbers and for that reason are mere-

ly approximations.

It can be concluded that (1) the bond energies in these organo-
tin molecules are additive and (2) in the compounds studied the
Sn-C bond energy has a reasonably constant value.

IV. INFRARED STUDIES

It has been the intention of the Physics Department at this
University to initiate a program of research in infrared spectros-
copy. In anticipation of this program, an investigation of the
infrared spectra of organo-tin compounds was undertaken on this
project. Since no instrument was available on this campus, samples
of the desired compounds were sent to e commercial laboratory where
spectrograms were made.

The data reported here are of a preliminary nature and the con-
clusions reached are tentative. Our own instrument has been recent-
ly purchased and as soon as it is installed this work will be ex-
tended.

Experimental

The compounds studied were prepared in a state of high purity
as described in an earlier section of this report. Spectrograms
of the compounds studied are shown in figures I and II. They in-
clude tetramethyl tin, I-A; tetraethyl tin, I-C; tetrapropyl tin
II-F; tetraphenyl tin I-E; tetra-n-amyl tin, II-H; tetra-n-hexyl
tin, I-D; tetraphenyl tin, I-B; diethyl tin dichloride, II-G; and
tripropyl tin chloride, II-J. In these figures the percent trans-
mission is plotted against wavelength and against wave number. In
the case of tetramethyl tin, the measurements made on samples of
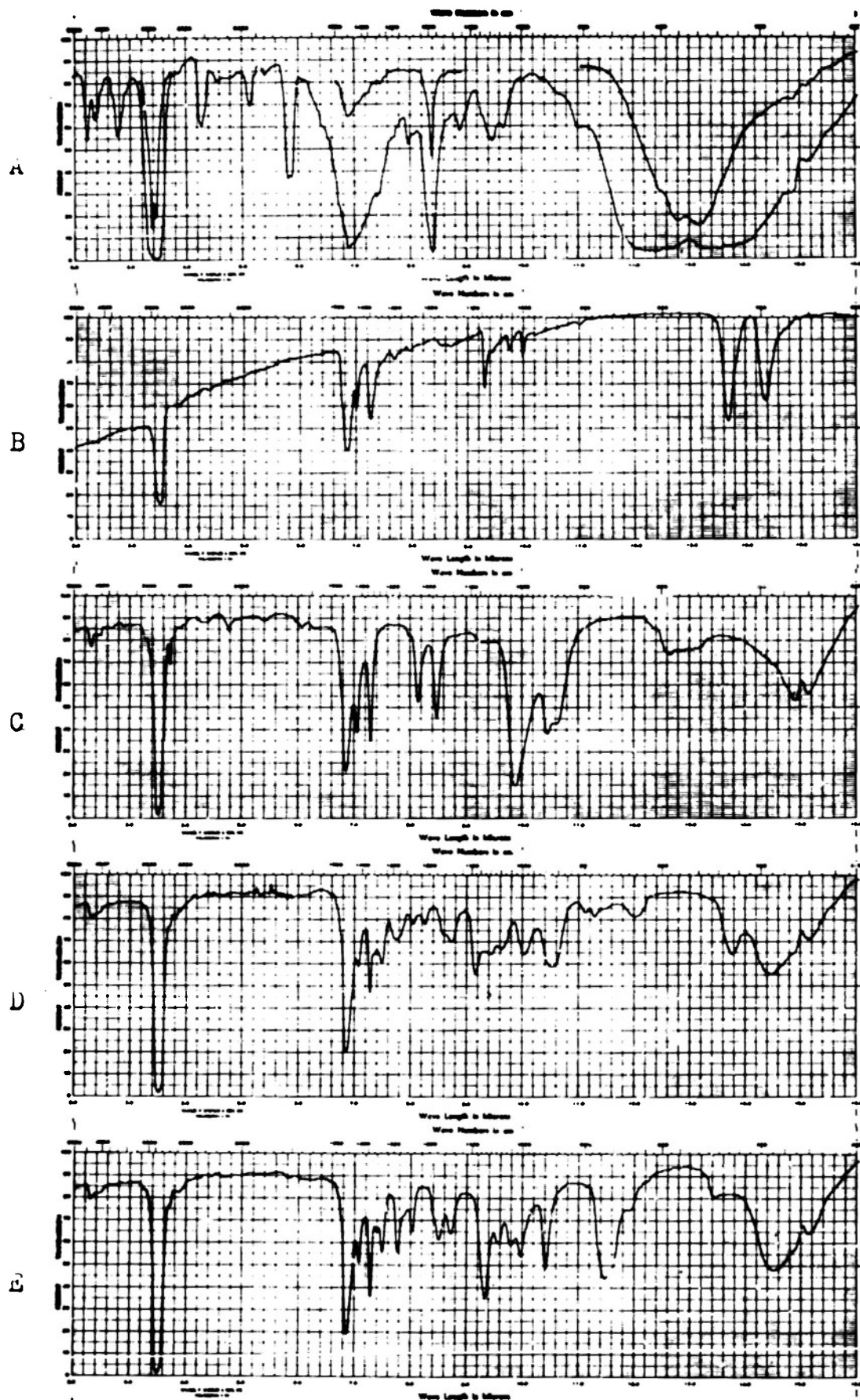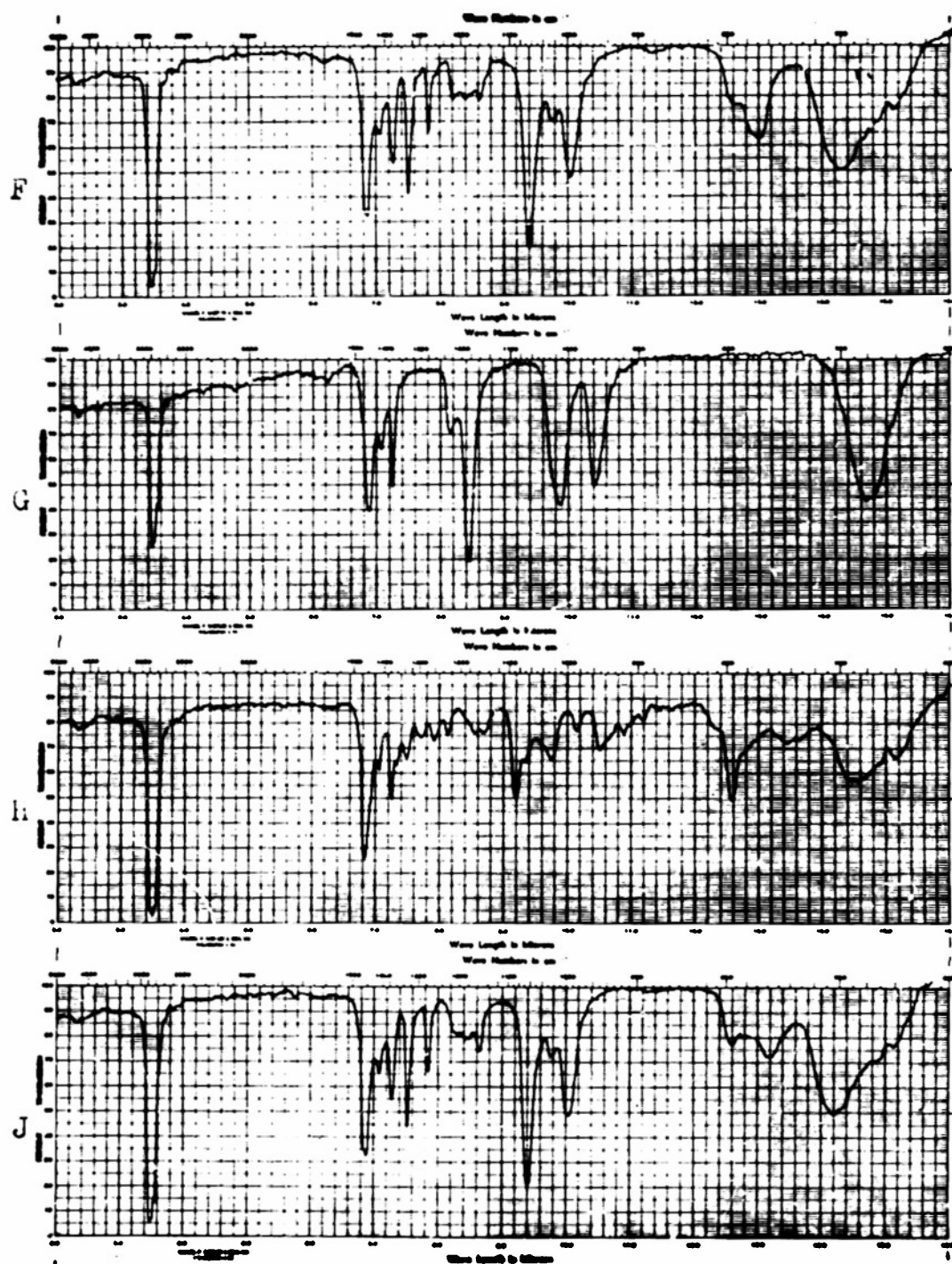0.2 mm. thickness and 0.01 mm. thickness are shown on the same
spectrogram.

FIGURE I.

FIGURE II.

The spectrograms were recorded at Samuel Sadtler and Son, Inc., employing a Baird Associates double beam spectrophotometer equipped with rock salt optics. The spectral region covered was from two to sixteen microns. The spectral slit widths extended from 0.003 inch to 0.17 inch. The position of the sharp absorption bands are determined to $\not< 0.025$ micron.

The spectra, with the exception of two samples, were obtained in the liquid state using Baird liquid cells with thickness of 0.01 and 0.20 mm. The spectrum of tetraphenyl tin was obtained in a Nujol mull. The spectrum of diethyl tin dichloride was run in a saturated carbon tetrachloride solution.

Analysis of the Spectrograms

A preliminary study has been made of the spectrograms of the six symmetrically substituted alkyl stannanes, SnR_4, where R indicates methyl, ethyl, propyl, butyl, amyl and n-hexyl groups successively.

This study was undertaken with the view of realizing the following objectives:

(1) to secure a unique physical characterization of these compounds by means of their infrared absorption spectra.

(2) to provide additional experimental evidence for the assumption that, even in complex molecules, certain molecular groupings of atoms retain their characteristic group vibrations.

(3) to observe the effect of the complexity of the substituent alkyl group in the compounds of the type SnR_4 upon the so called skeletal vibrations of molecules possessing this symmetry (T_d).

(4) to supply vibrational frequencies that may be used to calculate certain thermodynamical data for compounds of this type.[10]

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[10] E. B. Wilson, Chem. Rev. **17**, 27, (1940)

Of the compounds reported here, only tetramethyl tin has been previously studied spectroscopically.[11] A complete assignment of the fundamental frequencies of this compound has been made in the spectral region 1 to 15μ.[12]

[11]C. F. Kettering and W. W. Sleator, Physics $\underline{4}$, 39 (1933)
[12]C. W. Young, J. S. Koehler and D. S. McKinney, J. Am. Chem. Soc. $\underline{69}$, 1410 (1947)

The spectrogram of tetramethyl tin shown in Fig. I-A, is in exact agreement with that obtained by earlier workers,[11] therefore we have used the assignment of frequencies given by Young[12] and co-workers as a basis for assignments in the case of the higher members of this series. Also taken into account were the results of the analysis of the Raman spectra of tetraethyl silane[13] and the infrared analysis of tetraethyl lead[14] for which analogous vibrational frequencies should be expected.

[13]H. Murato, R. Okawara and T. Watase, J. Chem. Phys. $\underline{18}$, 1308, (1950)
[14]A. B. F. Duncan and J. W. Murray, J. Chem. Phys. $\underline{2}$, 636 (1934)

Preliminary assignments are listed in Table V, where ν (C-H) denotes stretching vibrations of the C-H bonds and δ (C-H) denotes deformation vibrations.

Consideration of the results from the point of view of the stated objectives of this investigation reveals the following:

(1) It is possible to uniquely characterize each of the compounds of the type SnR_4, by means of its infrared spectrum. A scrutiny of Figs. I and II reveals that the more significant spectral differences appear in the range 9 to 16 microns, the so-called "finger print region".

TABLE V

Preliminary Assignment of Group Vibrations

Compound	Observed Frequencies (cm^{-1})	
	ν (C-H)	δ (C-H)
Tetramethyltin	2906,2958	1449,1193, 781
Tetraethyltin	2849	1460,1416,1370, 1229,1180,790
Tetrapropyltin	2890	1456,1416,1377, 1333,1279,1218, 1190,1160,794 769,701
Tetrabutyltin	2857	1458,1412,1373,1333, 1289,1247,1176,1147, 745,690
Tetraamyltin	2857	1464,1416,1379,1366, 1337,1297,1263, 1232,1170,1152,743 691
Tetrahexyltin	2857	1460,1412,1374,1333, 1287,1244,1211,1163, 1145,727,691

(2) Table V reveals the degree to which CH_3 and CH_2 group vibrational frequencies are associated with stretching. $\nu(C-H)$, and deformation, $\delta(C-H)$, modes of vibrations remain invariant throughout the series of increasingly complex molecules, going from tetramethyl tin to tetra-n-hexyl tin.

(3) No skeletal vibrations appear in the spectral range embraced by the present survey.

These results indicate the necessity of extending the measurements over a wider spectral range (50 cm.$^{-1}$ to 5000 cm.$^{-1}$), and of re-examining the high frequency region under higher dispersion.

If this is done it should be possible to (1) make positive assignments of all observed frequencies on the assumption of a molecular model having symmetry T_d; (2) make an approximate calculation of the effective "R-masses", assuming that the radical behaves as a point mass[15,16]; (3) calculate force constants of Sn-C bonds in molecules of the type SnR_4.

[15]R. K. Sheline, J. Chem. Phys. 18, 602 (1950)
[16]R. K. Sheline and K. Pitzer, J. Chem. Phys. 18, 595 (1950)

V. ATTEMPTED PREPARATION OF CHLOROETHYL STANNANES

Several attempts were made to prepare chloroethyl tin chlorides of the general formula, $(Cl\ C_2H_4)_y SnCl_{(4-y)}$, where y is an integer, 1 to 4. Two methods of attack were employed: (1) photochemical chlorination with elementary chlorine in the presence of phosphorous pentachloride; (2) reaction with sulfuryl chloride in the presence of benzoyl peroxide.

Both procedures have been used successfully to prepare ana-

logous silicon compounds,[17,18,19] however in the case of the tin

[17]Ushakov and Itenberg, J. Gen. Chem. USSR 7, 2495 (1937)
[18]Krieble and Elliott, J. Amer. Chem. Soc. 67, 1810 (1945)
[19]Sommer and Whitmore, J. Amer. Chem. Soc. 68, 485 (1946)

compounds, replacement of the alkyl radical by chlorine rather than chlorination was the principal reaction.

When tetraethyl tin was used as the starting material a mixture of the ethyltin chlorides, stannic chloride and ethyl chloride were the only products. When ethyltin trichloride was used as the starting material, the products were stannic chloride and ethyl chloride.

In the case of the peroxide catalyzed reaction with sulfuryl chloride, a free radical mechanism was indicated. Ethane, ethylene, and butane were found among the gaseous reaction products. These were identified by measurement of their characteristic vapor pressures at several temperatures, and by determination of their molecular weights. Since the experiments were not designed to collect these substances quantitatively, it is not possible to report exact yields. In as much as in no case were the desired chloroethyl tin chlorides obtained, this phase of the investigation was discontinued.

VI. SOME PROPERTIES OF ETHYLTIN CHLORIDES

In order to separate and identify possible products in the chlorination experiments, it was necessary to collect data on the physical properties of the ethyl tin halides. Little such information is found in the current chemical literature. Therefore, very pure samples of these compounds were prepared and a careful study of their physical properties was made.

The results of these studies are summarized in Table VI. Those properties not previously reported in the literature are denoted by asterisks.

Experimental

The ethyl tin chlorides were prepared by refluxing, according to the method of Kocheshkow[20], calculated amounts of anhydrous

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[20]Kocheshkow, Ber, __66__, 1661, 1933.

---

stannic chloride and tetraethyl tin for 10-12 hours. Purification of the crude materials was achieved by repeated fractionation through a small Vigreaux column until products were obtained which showed no change in refractive index upon further distillation and which, upon analysis for tin and chlorine, agreed within 1% of the theoretical.

Anal. Calc. for $C_2H_5SnCl_3$; Sn, 46.9; Cl, 41.8. Found Sn, 46.1
Cl, 41.2. Calc. for $C_4H_{10}SnCl_2$; Sn, 48; Cl, 28.6
Found: Sn 47.8; Cl 29.0. Calc. for $C_6H_{15}SnCl$; Sn, 49.2;
Cl, 14.7. Found: Sn, 48; Cl, 14.7.

The densities of the liquid compounds were measured with a precision of .001 g/ml. at $20 \pm 0.1^\circ$ C. The melting points of the liquid samples were determined from cooling curves and the melting point of the solid diethyl tin dichloride was determined in a capillary tube in the conventional manner. The vapor pressures were determined by the boiling point method, the external pressure being maintained constant within ± 0.5 mm. Plots of $\log_{10} P$ versus $(1/T)$ were linear from 10 mm. to atmospheric pressure.

Molecular refractions were calculated using the atomic refrac-

TABLE VI

Physical Properties of Ethyl Tin Chlorides

Formula	Density g/ml at 20°	Ref. Index n_D^{20}	Mole Refraction Calcd	Mole Refraction Found	Melting Point °C	Vapor Pressure Equation Constant[a] A	B	Calcd. B. Pt. °C at 760 mm	Calcd. Heat of Vaporization cal/mole	Trouton's Const. cal/mole degree
$C_2H_5SnCl_3$	1.965	1.5408*	41.80[c] (40.22)[d]	40.61*	<10°*	2554*	8.377*	192 (196)[b]	11672*	25.1*
$(C_2H_5)_2SnCl_2$					84°	2753*	8.385*	227 (220)[b]	12581*	25.2*
$(C_2H_5)_3SnCl$	1.429	1.5055	50.54[c] (50.20)[d]	50.15	15°	2652*	8.416*	206 (230)[b]	12119*	25.3*

[a] constants for the equation $\log_{10} P = -\frac{A}{T} + B$;

[b] previously reported values (Ref 20);

[c] calculated from atomic refractions;

[d] calculated from bond refractions;

tions of carbon, hydrogen and chlorine given by Eisenlohr,[21] and

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[21]F. Eisenlohr, Z Physik Chem. <u>75</u>, 585 (1910).

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that of tin given by Jones and co-workers[1] (loc. cit.) as determined in tetraethyl tin.

Since the value of the atomic refraction of tin varies with the nature of the groups to which it is attached, the agreement of the observed values of the molar refraction with the calculated values is as good as can be expected.

Recently, West and Rochow[22] have devised a system of bond re-

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[22]R. West and E. G. Rochow, J. Am. Chem. Soc., <u>74</u>, 2490 (1952)

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fractions for tin compounds. Using appropriate values from their list and the C-C and C-H bond refractions of Denbigh,[23] calculated

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[23]K. G. Denbigh, Trans. Faraday Society, <u>36</u>, 936, (1940)

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molecular refractions are obtained which are in excellent agreement with the experimental values.

VII. PREPARATION OF ETHYL STANNANES

Finholt and co-workers[24] have described the preparation of

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[24]A. E. Finholt, A. C. Bond, Jr., K. W. Wilzbach and H. I. Schlesinger, J. Am. Chem. Soc. <u>69</u>, 2692, (1947).

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methylstannanes by the reaction of lithium aluminum hydride with the appropriate methyltin halide according to the general equation

$$4 \ R_ySnX_{(4-y)} + (4-y)LiAlH_4 \longrightarrow 4 \ R_ySnH_{(4-y)} + (4-y)LiX + (4-y)AlX_3$$
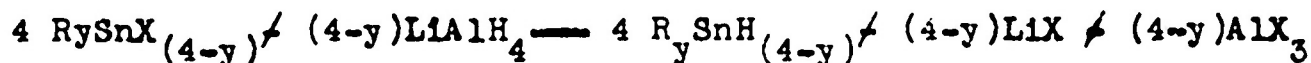
where R represents the methyl radical, X represents a halogen and y is an integer, 1, 2, or 3. It is implied that this procedure can be applied to the preparation of analogous compounds where the

radical, R, may represent any alkyl or aryl group.

However, in this investigation, it has been observed that there are two factors which limit the application of this procedure in the case of the organo stannanes. These factors are as follows:

(1) There is a large difference between the volatilities of the methyl stannanes and stannanes containing heavier radicals. This difference is comparable to that observed between tetramethyl tin, (normal B. Pt. 78° C), and tetraethyl tin, (normal B. Pt. 177° C). Consequently, higher distillation temperatures are required for purification of the higher alkyl stannanes even when the pressure is reduced. This results in considerable decomposition of these inherently unstable compounds.

(2) It has been observed that lithium aluminum hydride attacks the alkyl radicals as well as the halogens of the alkyl tin halide. The products of this side reaction are, hydrogen, hydrocarbons, polymeric solids and metallic tin. The amount of side reaction is quite appreciable at and above room temperature. It has also been demon-strated that tetraethyl tin reacts with lithium aluminum hydride to give similar products.

Because of the above mentioned difficulties, only the ethyl stannanes have been prepared in quantities sufficient for a study of their properties.

Experimental

The procedure followed was essentially that described by Finholt[24] (loc. cit.). In the preparation of triethyl stannane and diethyl stannane, diethyl ether was used as a solvent and the products were purified by distillation through a small Vigreaux column

under reduced pressure. In the preparation of ethyl stannane, dibutyl ether was used as the solvent and the product was purified by fractional condensation on a vacuum line.

The identities of the compounds were established by molecular weight determination and by analysis for tin and hydrolyzable hydrogen. Physical properties studied included vapor pressure, refractive index, and density. The individual compounds and their properties are described below.

<u>Triethyl Stannane</u>: Calcd. for $(C_2H_5)_3SnH$: Sn 57.48; hydrolyzable H, 0.487%. Found: Sn, 56.2; hydrolyzable H, 0.49%. Density, 1.258 g/ml at 20° C. n_D^{20} = 1.4700. Vapor pressures were determined by the boiling point method. The plot of log P versus $(1/T)$ was linear in the pressure range between 10 and 200 mm. and is represented by the equation, $\log_{10}P = -2273/T + 8.36$. By extrapolation, the normal boiling point was found to be 142° C.

<u>Diethyl Stannane</u>: Calcd. for $(C_2H_5)_2SnH_2$: M. Wt., 178.7; hydrolyzable H, 1.1%. Found: M. Wt., 176; hydrolyzable H, 1%. Vapor pressures were measured on the vacuum line. The best straight line through fourteen points is represented by the equation, $\log_{10}P = -2041/T + 8.67$. By extrapolation the normal boiling point was found to be 81° C.

<u>Ethyl Stannane</u>: Calcd. for $(C_2H_5)SnH_3$: M. Wt., 150.7; hydrolyzable H, 1.9%; C_2H_5-, 19.3%. Found: M. Wt., 150.5; hydrolyzable H, 1.7%; C_2H_5 - 19%. Vapor pressures were measured on the vacuum line. The best straight line through thirteen points is represented by the equation, $\log_{10}P = -1470/T + 7.65$. The normal boiling point was calculated to be 34° C.

VIII. SUMMARY

As a result of this investigation, several signigicant differences between the organic derivatives of stannane and those of analogous compounds of carbon and silicon have become apparent. In every case these differences may be attributed to the more electropositive nature of tin.

(1) Carbon-carbon, (C-C), and silicon-carbon, (Si-C), "bond energies" estimated by Pauling,[9] (loc. cit.) are 58.6 kcal/mole and 57.6 kcal/mole, respectively. The closeness of these values indicates a similarity in bond type in these cases. The tin-carbon, (Sn-C), "bond energies" computed in this investigation by analogous procedures is about 35 kcal/mole. Thus a profound difference in bond type between this and the former cases is indicated.

(2) No important skeletal vibrations were observed in the spectral region covered by the infrared studies reported here. It might be expected that, in the case of tetraethyl tin and higher alkyl stannanes, an absorption band would occur at 900 cm^{-1} since this is a characteristic C-C stretching frequency.[25] Failure to observe

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[25] G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, New York, 1945, page 195.

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such a band in the spectra of these compounds may be due to the change in moment produced by the presence of tin as the central atom.

(3) The unsuccessful attempts to prepare chloroethyl stannanes, by methods used to prepare analogous compounds of silicon, is further evidence of a difference in bond type. Owing to the large difference in electronegativity between tin and carbon, cleavage of the alkyl group with the formation of tin halides was the predominant reaction.

(4) The relative electronegativity of the elements is a particular-
ly important factor in the preparation of hydrides. For example,
it has been observed that if the electronegativity of a metal is
less than 1.5 on Pauling's scale,[26] the hydride of the metal may

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[26]L. Pauling (loc. cit.) page 64.

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be prepared by the reaction of lithium aluminum hydride with an
alkyl derivative; whereas the metal chloride either does not react
with lithium aluminum hydride or is reduced to free metal by this
reagent. On the other hand, elements having an electronegativity
greater than 1.5 on Pauling's scale yield hydrides when the chloride
is reacted with lithium aluminum hydride while the alkyl deriva-
tives are unaffected. It appears that the element, tin, is unique
in that both alkyl groups and chlorine in alkyltin chlorides are
attacked by lithium aluminum hydride. Only by careful control of
the temperature can the halogen be replaced by hydrogen exclusive
of side reactions. This suggests that the electronegativity of tin
is considerably less than the value of 1.7 given in Pauling's table.

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